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Exciplexes of Polycyclic Aromatic Hydrocarbons with Halomethanes

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The fluorescence spectra of polycyclic aromatic hydrocarbons such as anthracene, 1,2-benzanthracene, 2,3-benzanthracene and 1,2,5,6-dibenzanthracene quenched by halomethanes, reveal shift in fluorescence band. Both Stern-Volmer constants for fluorescence quenching and fluorescence band shifts are linearly related to the difference of ionization potential and first excited singlet energy of aromatic hydrocarbons.

Recently we have reported[1] the formation of contact charge transfer (CT) pair in heptane solvent and thermodynamic and spectrophotometric properties of the 1:1 (CT) pairs in heptane solution, between different polycyclic aromatic hydrocarbons, namely anthracene, 1,2-benzanthracene (tetraphene), 2,3-benzanthracene (tetracene) and1,2,5,6-diabenzanthracene (as donors) and halomethanes such as carbon tetrachloride, chloroform and dichloromethane (as acceptors). There are several reports[2-12] of fluorescence quenching of aromatic hydrocarbons by halomethanes in solution as well as in gas phase and of photoreactions involving exciplexes of reactant species. Electron donor-acceptor (EDA) interaction between two dissimilar molecules when one of them is in electronically excited state gives rise to familiar exciplex emission. In the majority of reported cases, polycyclic aromatic hydrocarbons acted as electron acceptors and the electron donor molecules invariably contained one or more heteroatoms like nitrogen or oxygen[13-17] and one of the lone pair electron was transfered to the excited aromatic hydrocarbon molecule during exciplex formation. To understand EDA properties of these polycyclic aromatic hydrocarbons in the excited state interaction with halomethanes, the fluorescence spectra of these aromatic hydrocarbons in the presence of halomethanes have now been studied.

Materials and Methods

Aromatic hydrocarbons (Aldrich Chemicals, USA), listed in Table 1, were purified by recrystallization from benzene. Spectrograde (BDH) halomethanes and heptane were used as such; except chloroform which was purified by standard method. Because of the sparing solubility of these hydrocarbons in heptane, except that of anthracene, the solutions of these aromatic hydrocarbons were prepared by dissolving these in benzene. An aliquot from benzene solution was dried in the dark under nitrogen atmosphere and to it was added a measured volume of heptane to get the required concentration. All solutions were always prepared afresh in the dark to avoid photochemical change.

Fluorescence spectra of these solutions were recorded on a Perkin-Elmer MPF-44B spectrofluorimeter using fused silica cell of 1 cm optical path length.

Results and Discussion

The fluorescence spectra of anthracene in different solvents at 25°C are presented in Fig. 1; other aromatic hydrocarbons showed similar behaviour in

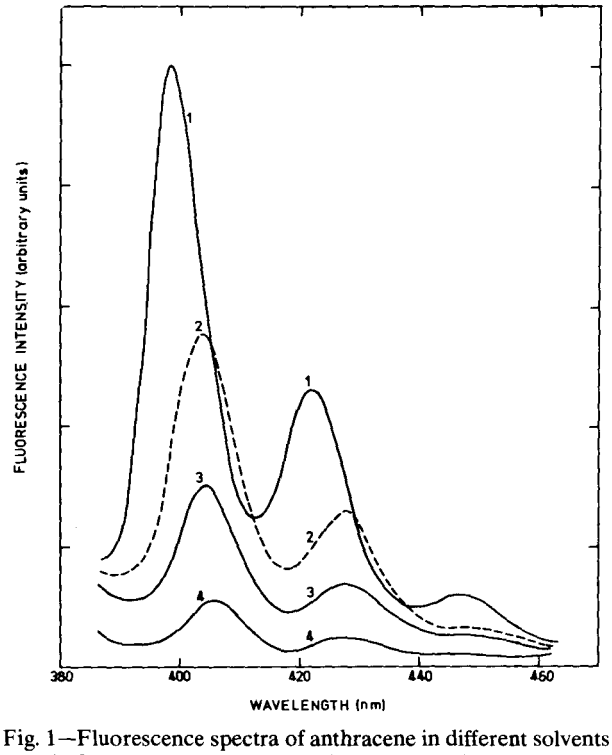

Fig. 1—Fluorescence spectra of anthracene in different solvents at 25°C [Solvents are: (1) heptane, (2) CH_2Cl_2, (3) $CHCl_3$ and (4) CCl_4. Concentration of anthracene is 1.067×10^{-4} mol dm^{-3} in all cases]

Table 1—Fluorescence Maxima of Aromatic Hydrocarbons in Different Solvents with Ionization Potentials (I_D) and First Excited Singlet Energies (S_1) of Aromatic Hydrocarbons

Aromatic hydrocarbon	I_D^* (e.V)	S_1^* (eV)	$\tilde{\nu}_{max}$ (cm^{-1}) in solvent†			
			Heptane	CH_2Cl_2	$CHCl_3$	CCl_4
Anthracene	7.12	3.32	25094	24814 (280)	24752 (342)	24691 (403)
Tetraphene	7.35	3.22	24540	24390 (150)	24361 (179)	24331 (209)
Tetracene	6.64	2.63	19822	19592 (230)	19524 (298)	19507 (315)
Dibenzanthracene	7.42	3.14	25409	25288 (121)	25268 (141)	25252 (157)

*Values of I_D and S_1 are taken from refs. 20 and 19 respectively.
†Figures in parentheses represent spectral shifts on going from heptane to halomethane.

Table 2—Stern-Volmer Quenching Constants of Tetracene-Halomethane and Carbon Tetrachloride-Aromatic Hydrocarbon Systems at 25°C

Tetracene (4.108×10^{-5})		Carbon tetrachloride (0.21-1.04)	
Halomethane	K_{SV} ($dm^3\ mol^{-1}$)	Aromatic hydrocarbon	K_{SV} ($dm^3\ mol^{-1}$)
CH_2Cl_2 (0.31-1.56)	0.106	Anthracene (9.56×10^{-5})	0.641
$CHCl_3$ (0.25-1.25)	0.147	Tetraphene (5.87×10^{-5})	0.106
CCl_4 (0.21-1.04)	0.164	Tetracene (4.108×10^{-5})	0.164
		Dibenzanthracene (4.11×10^{-5})	0.049

Figures in parentheses indicate concentration in mol dm^{-3}.

these solvents. The fluorescence band positions of the aromatic hydrocarbons in different solvents are recorded in Table 1. It is evident from Table 1 that the fluorescence band of all the aromatic hydrocarbons undergoes shift on going from heptane to halomethane. This shift linearly increases with increasing ionization potential of halomethane but it is not related to the ionization potential of aromatic hydrocarbon. However a good linear relationship is obtained between spectra shift ($\Delta\nu$) and difference in ionization potential and first excited singlet energy ($I_D - S_1$) of aromatic hydrocarbon (Fig. 2).

By measuring the decrease in relative quantum yields of aromatic hydrocarbons (excited at the longest wavelength absorption band in heptane) at varying concentrations of halomethanes in heptane, the Stern-Volmer quenching constant, K_{SV} has been calculated using the relation[18] (1).

$$\frac{\phi_f^o}{\phi_f} = 1 + K_{SV}[A] \qquad \ldots(1)$$

where ϕ_f^o and ϕ_f are the relative quantum yields of

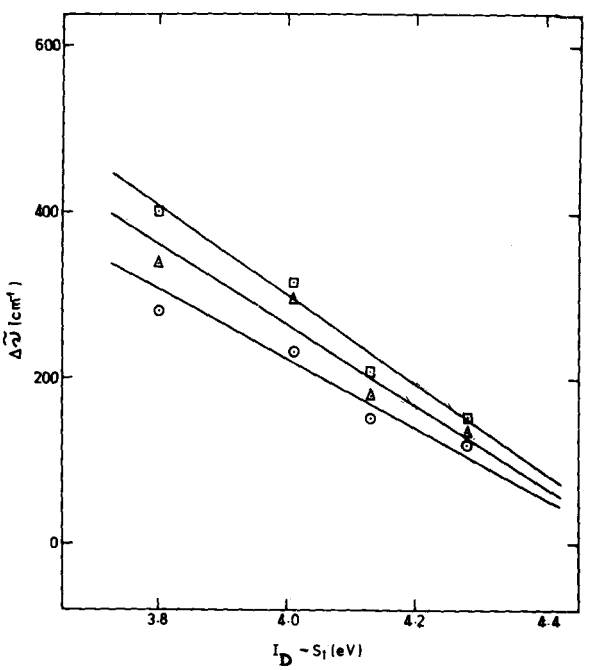

Fig. 2—Correlation between the spectral shift ($\Delta\tilde{\nu}$) of fluorescence bands of aromatic hydrocarbons in different halomethanes and ($I_D - S_1$) of aromatic hydrocarbons [Each curve represents four aromatic hydrocarbons with one halomethane: CH_2Cl_2 (○), $CHCl_3$ (△) and CCl_4 (□)]

fluorescence for aromatic hydrocarbons alone and in the presence of halomethane (A) respectively; [A] is the molar concentration of halomethane. The plots of ϕ_f^o/ϕ_f against [A] are all linear (Figs 3 and 4), from the slopes of which K_{SV} values are calculated. The values of K_{SV} of different aromatic hydrocarbons with carbon tetrachloride as well as of different halomethanes with tetracene are presented in Table 2.

The red-shift in the fluorescence spectra of aromatic hydrocarbons in halomethanes in addition to the normal quenching may be due to the formation

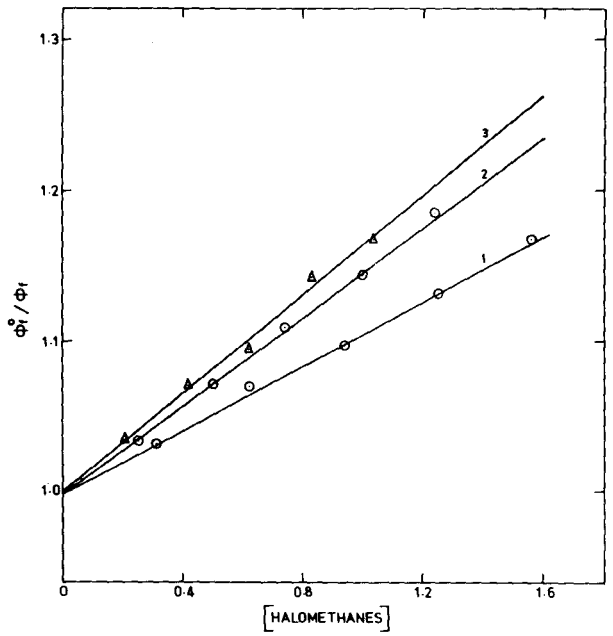

Fig. 3—Spectrofluorimetric determination of Stern-Volmer quenching constants (K_{SV}) of tetracene-halomethanes in heptane at 25°C [Halomethanes are: (1) CH_2Cl_2, (2) $CHCl_3$ and (3) CCl_4. Concentration of tetracene: 4.108×10^{-5} mol dm^{-3} and concentration range of halomethanes: 0.2-1.5 mol dm^{-3}]

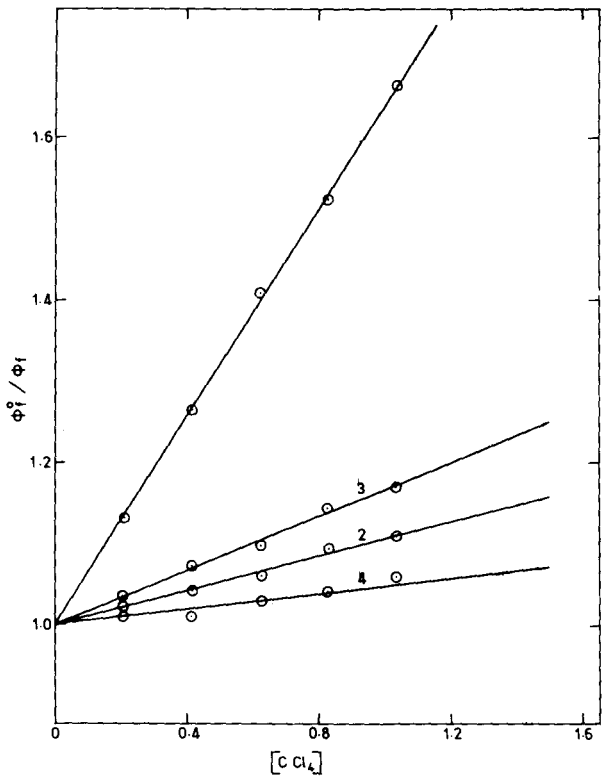

Fig. 4—Spectrofluorimetric determination of Stern-Volmer quenching constants (K_{SV}) of aromatic hydrocarbon-CCl_4 in heptane at 25°C [Aromatic hydrocarbons with concentration (mol dm^{-3}): (1) anthracene (9.56×10^{-5}), (2) tetraphene (5.87×10^{-5}), (3) tetracene (4.108×10^{-5}), (4) dibenzanthracene (4.11×10^{-5}). Concentration range of CCl_4: 0.21-1.04 mol dm^{-3} in all cases]

of exciplexes, i.e. complexes between the excited aromatic hydrocarbons and the halomethane molecules which break up shortly after formation either with the emission of the characteristic spectrum or through nonradiative pathway. If this emission is due to exciplex formation, one would expect a relationship of the type represented by Eq. (2), between the frequency (ν_f) of emission and other molecular parameters[19]

$$h\nu_f = (I_D - S_1) - E_A - \Delta \quad \ldots(2)$$

In Eq. (2) I_D and S_1 are respectively the ionization potential and the first singlet excited state energy of aromatic hydrocarbons, E_A is the electron affinity of halomethanes and Δ represents the various other interaction terms. As the plot of ν_f against $I_D - S_1$ or I_D is nonlinear, the emission bands are the red-shifted normal fluorescence bands due to exciplex formation and not due to exciplex emission or emission from ground state CT complexes. The exciplex emission is expected at longer wavelength which is not observed in these systems. The increase in red-shift of fluorescence band, $\Delta\bar{\nu}$ with increase in ionization potential of halomethanes as well as with decreasing magnitude of $(I_D - S_1)$ of aromatic hydrocarbons suggests that halomethanes act as electron acceptors and aromatic hydrocarbons as electron donors. The donor capacities of aromatic hydrocarbons follow the order: anthracene > tetracene > tetraphene > dibenzanthracene; while the acceptor capacities of halomethanes are in the order: carbon tetrachloride > chloroform > dichloromethane. This supported by the corresponding values of Stern-Volmer quenching constants of these systems.

The Stern-Volmer quenching constants are measured at low concentrations of halomethanes, since at higher concentrations, a curvature in Stern-Volmer plots is obtained. The curvature indicates ground state complexes[9] and the formation of ground state complexes in these systems is verified by the studies of absorption spectra[1].

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